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Geoffroy Gadacz, Sorina Udriou, Jean-Paul Viricelle, Christophe Pijolat, Michèle Pijolat. Nickel based anodes for single chamber solid oxide fuel cells : a catalytic study. ECS Transactions, 2009, 19 (17), pp.59-70. 10.1149/1.3242369 . hal-00494465

**HAL Id: hal-00494465**

**<https://hal.science/hal-00494465>**

Submitted on 23 Jun 2010

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## Nickel based anodes for single chamber solid oxide fuel cells : a catalytic study

Geoffroy Gadacz, Sorina Udriou, Jean-Paul Viricelle, Christophe Pijolat, Michèle Pijolat

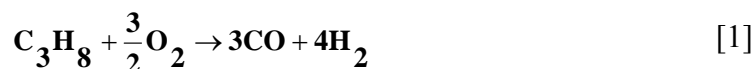
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Single chamber solid oxide fuel cells (SCFC) are an alternative concept to traditional SOFC's. Conventional anodes, which consist of a cermet of metallic Ni and ionic conductor, have to work under a mixture of hydrocarbon and oxygen. This paper presents a catalytic study of C<sub>3</sub>H<sub>8</sub> oxidation by Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> and nickel. The influence of temperature and oxygen to propane ratio on the nickel oxidation state are clarified thanks to catalytic tests and electrical conductivity measurements. The results show that the temperature must be higher than a critical value in order to maintain the nickel particles in the metallic state. Furthermore, at high temperature, the conversion of the initial mixture leads to the water-gas-shift equilibrium.

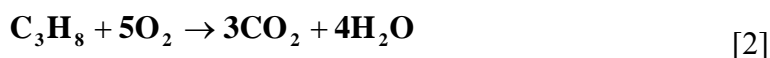
### Introduction

Fifteen years ago, Hibino (1) has shown the feasibility of a fuel cell consisting of only one chamber, with a mixture of reducing and oxidizing gases (generally hydrocarbon and oxygen). This concept allows avoiding the sealing procedure of traditional fuel cell, and a better control of gases. Single Chamber Fuel Cells (SCFC's) have quickly shown good results, close to traditional SOFC's power densities (2-7). Some research groups nevertheless reported some drawbacks such as voltage oscillation and nickel-based anode instability (8). They attributed these oscillations to oxidation/reduction cycles of the metal. However, to our knowledge, very few studies have been devoted to the anode properties in the working conditions of SCFC's.

Traditional anodes consist of a cermet, based on a solid ionic conductor (for example GDC: Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub>) mixed with an electronic conductor, such as metallic nickel. They are generally used in hydrogen, which is easily dissociated in presence of metallic nickel. Because of the problems involved by the direct use of H<sub>2</sub>, an alternative way is to use the catalytic partial oxidation of hydrocarbons, leading to a mixture of CO and H<sub>2</sub>. An example is given by the partial oxidation of propane [1] ( $\Delta H^\circ$  (850K) = -206 kJ.mol<sup>-1</sup>):



Nickel is known to have a good catalytic activity for this reaction (9) ; the exothermicity of the reaction helps to maintain the temperature of the cell, and the oxygen partial pressure limits the carbon deposition. But, using propane with oxygen may induce an undesirable reaction [2] ( $\Delta H^\circ$  (850K) = - 2043 kJ.mol<sup>-1</sup>) which consists of the direct total oxidation:



The conditions of stability of metallic nickel versus its oxidation into NiO, and competition effects between reactions [1] and [2] have to be clarified for achieving a good SCFC efficiency. In this paper, we present first the catalytic activity and stability of GDC and Ni powders in presence of propane and oxygen mixtures. Then, the variation of the electrical conductivity of Ni-GDC anodes is reported as a function of temperature in presence of a mixture of propane and oxygen. The results are interpreted on the basis of the oxidation state of nickel together with its catalytic properties.

## Experimental

### Samples

GDC ( $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ ) was supplied by Fuel Cell Materials<sup>TM</sup> (Nextech<sup>TM</sup> division). Its specific surface area, measured using BET method with nitrogen (Micromeritics ASAP 2000) was  $8 \text{ m}^2.\text{g}^{-1}$ . The average particle size corresponding to this area surface is  $0.1 \mu\text{m}$ , assuming spherical particles of a same size. The powder was then characterized by laser granulometry (Malvern Mastersizer 2000), as presented in figure 1. The particle size distribution of GDC powder as supplied showed three maxima at 1, 5 and  $110 \mu\text{m}$ . A sieving procedure at  $100 \mu\text{m}$  was able to eliminate the largest agglomerates.

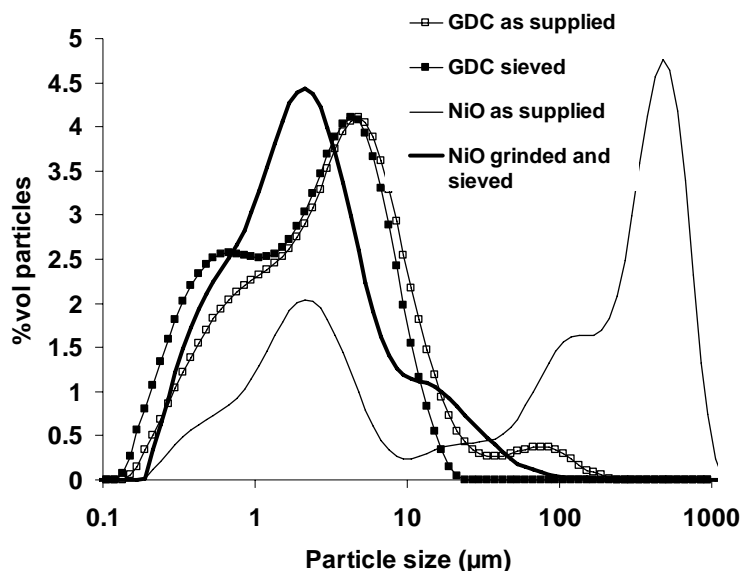


Figure 1 : Laser granulometry study of the initial and treated GDC and NiO powders

NiO was supplied by Sigma-Aldrich<sup>TM</sup>. Its BET specific surface area was equal to  $5 \text{ m}^2.\text{g}^{-1}$ , corresponding to a particle size of  $0.13 \mu\text{m}$ , which is very close to that of GDC. Laser Granulometry analyses see figure 1 revealed a very broad particle size distribution with various maxima, the most important being at 4 and  $500 \mu\text{m}$ . To lower the NiO average particle size, a grinding procedure has been applied using a planetary ball mill (stainless steel balls) at 180 rpm for 30 min. XPS analyses after treatment did not show any pollution of the surface due to grinding. Laser granulometry analyses show that all the agglomerates have been broken into aggregates smaller than  $100 \mu\text{m}$ . Sieved GDC or ground and sieved NiO will be referred as “treated” powders in the following.

### Catalytic activity

The treated powders were mixed with alpha-alumina powder from Alpha-Aesar<sup>TM</sup> to obtain samples of 10 (or 20%wt) of NiO or GDC. Alpha-alumina was used in order to minimize over temperature effects due to the exothermicity of reactions (1) and (2). This powder was also inert with respect to the gaseous mixtures.

The catalytic activity was measured in a catalytic reactor equipped with a tubular 10 mm diameter quartz tube. Quartz wool was placed in the middle of the tube to support the sample, allowing a fixed bed reactor. A thermocouple protected by an alumina tube to avoid catalytic artefacts was fixed near the powder. The tube was introduced inside a vertical furnace whose temperature was regulated by a thermocouple placed near to the sample bed. A condenser at the outlet of the tube allowed to trap water before gas analyses. The composition of the gaseous mixture was then determined with a micro-gas chromatograph coupled with a mass spectrometer (SRA instruments<sup>TM</sup>). The different partial pressures of the system were calculated using calibrated gases. It allows to determine partial pressures of around  $10^{-2}$  atm with a precision of  $\pm 10^{-4}$  atm.

Prior to the catalytic activity measurements, the GDC /  $\alpha$ -alumina mixtures were heated at 580°C and maintained during 1h at this temperature in order to eliminate adsorbed species from the surface. In case of NiO /  $\alpha$ -alumina mixtures, a reduction step treatment in hydrogen (2% H<sub>2</sub> in Ar at 10 l.h<sup>-1</sup>) was first done at 580°C during 3 hours in order to transform NiO particles into metallic nickel. Then, once the desired temperature was established under flowing argon, O<sub>2</sub> / C<sub>3</sub>H<sub>8</sub> / Ar was introduced in the reactor ( for example 0.6 / 0.4 / 9 l.h<sup>-1</sup> respectively) and the catalytic activity was measured after a stabilization period of one hour, during which the reactor reaches a constant value after an initial increase due to the exothermicity of the reactions. Temperature tests were done by decreasing temperature after the stabilization time at a fixed ratio, with a constant ramping rate of 1°C.min<sup>-1</sup>. Gas analyses were done every ten minutes, corresponding to a measure every ten degrees.

In all the experiments, the amount of propane and oxygen never exceeded 10% of the gaseous phase for two reasons. First, it ensured that whatever the ratio O<sub>2</sub> / C<sub>3</sub>H<sub>8</sub> could be, the reactor gaseous atmosphere was far from exploding conditions ; second at low partial pressures, the volume expansion of the gas due to the reactions is low and thereby the errors of outlet quantitative analysis. The various O<sub>2</sub> : C<sub>3</sub>H<sub>8</sub> volumic ratios were comprised between 1:9 and 9:1 in argon and the total flow rate was fixed to 10 l.h<sup>-1</sup>, for all experiments. In the following the notation x / 10-x will be used for the oxygen to propane ratio, which means x % of oxygen and (10-x) % of propane in the gaseous mixture.

### Electrical conductivity

Four points measurements of the electrical conductivity of Ni – GDC cermet supported on GDC pellets were done in order to follow the oxidation state of nickel as a function of temperature in the O<sub>2</sub> / C<sub>3</sub>H<sub>8</sub> / Ar mixture.

First, a GDC support was prepared from the treated powder by sintering at 1200°C for 6 hours, then at 1350°C for 4 hours a pellet previously pressed at 100MPa. The initial

and final diameter of the pellet was 22mm and 19mm respectively; the thickness of the sintered pellet was 1.5mm. The Ni-GDC cermet was deposited onto the GDC sintered pellet using screen-printing technology. First, treated powders were mixed using 60%wt of NiO and 40%wt of GDC, then a commercial binder and a solvent (supplied by ESL Europe) were added. The final ink was shaken using an UltraTurrax™ for 20 min.

After deposition due to an Aurel™ device, we obtained a homogeneous layer whose thickness was 25µm. Four platinum contacts located on the edges of the cermet, allowed to monitor the electrical conductivity according to the Van der Pauw method, with a current source of  $I = \pm 50\text{mA}$  (Keithley Sourcemeter 2600C). The sample was placed in a tubular furnace equipped with a quartz tube of 3 cm diameter.

The NiO-GDC as prepared cermet anode was treated with the same conditions as for the catalytic powder reactor in order to achieve the reduction of NiO into metallic Ni. Then the electrical conductivity of the sample was measured for various temperatures under a flowing 6 / 4 ratio at  $20 \text{ l.h}^{-1}$ .

X-ray diffraction (Siemens D5000) has been used to characterize the samples after the catalytic activity and electrical measurements. The X-ray emission has been done with a copper anticathode. The detector is a scintillator with a graphite monochromator.

## Results and discussions

### Catalytic activity

#### GDC results

The results concerning GDC catalytic activity at 590°C (sample mass: 15 mg of GDC mixed with 85mg of  $\alpha\text{-Al}_2\text{O}_3$ ) are presented in figure 2 as a function of the  $\text{O}_2 / \text{C}_3\text{H}_8$  ratio. It can be seen that the maximum catalytic activity is reached at 6-7% of  $\text{O}_2$  (and respectively 4 and 3% of  $\text{C}_3\text{H}_8$ ), leading to a high production of carbon dioxide. This maximum suggests that the major reaction taking place in this case is the total oxidation of propane, producing  $\text{CO}_2$  and  $\text{H}_2\text{O}$  according to reaction [2]. Effectively, the stoichiometric proportions of this reaction would correspond to an  $\text{O}_2 / \text{C}_3\text{H}_8$  ratio equal to 8.33 / 1.67 which is near to the experimental observed ratio. In addition to this reaction, it can be observed a small quantity of CO and  $\text{H}_2$  corresponding to the propane partial oxidation, according to reaction [1]. The maximum amount for these gases is observed around 6 / 4 oxygen to propane ratio, which is in agreement with the stoichiometric proportions of reaction [1]. Finally, some  $\text{C}_2\text{H}_4$  and  $\text{CH}_4$  could be observed, especially at low  $\text{O}_2 / \text{C}_3\text{H}_8$  ratios. Both products were also identified during a blank test (without any powder in the reactor) showing that propane cracking takes place in the gas phase, according to reaction [3]



$\text{CH}_4$  was not detected for most of the ratios, probably because it is readily oxidized.

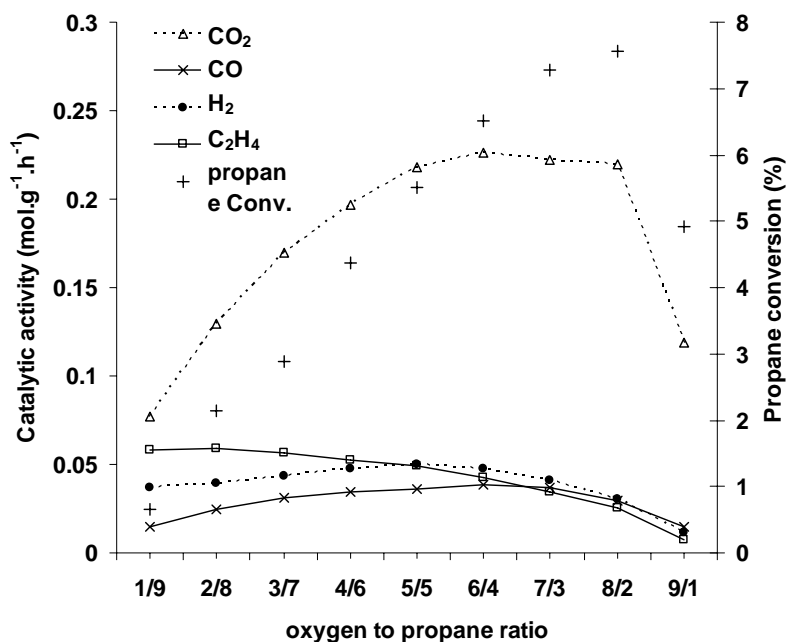


Figure 2: Catalytic activity of GDC (15 mg; 10%wt in alumina) at 590°C, as a function of the O<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> ratio.

Figure 3 presents the catalytic activity of GDC as a function of temperature obtained for a 6 / 4 oxygen to propane ratio. It can be seen that the catalytic activity increases with the temperature increase. The maximal conversion for propane and oxygen was 9 and 22 % respectively, the major reaction product being CO<sub>2</sub> for all temperatures. Arrhenius plot deduced from the CO<sub>2</sub> catalytic production leads to a value of the apparent activation energy equal to 75 kJ.mol<sup>-1</sup>. Other temperature tests have shown good reproducibility, by starting measurements at low temperature, and applying a increasing ramping rate of 1°C.min<sup>-1</sup>.

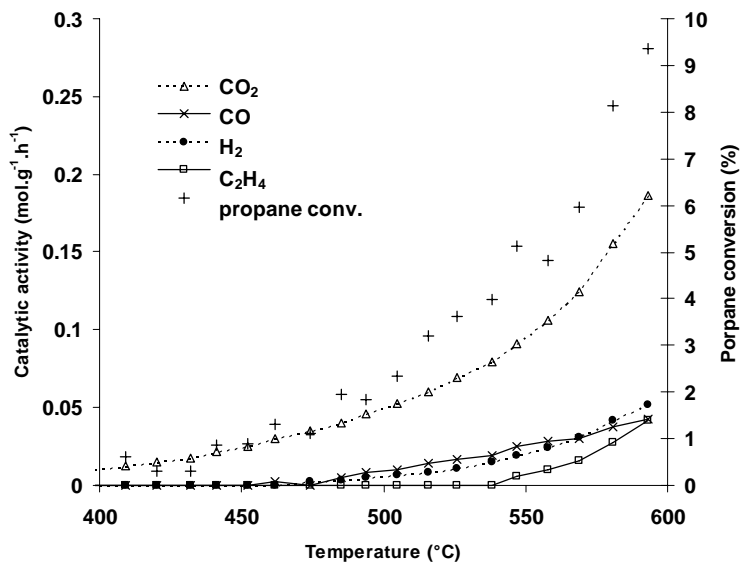


Figure 3: Catalytic activity of GDC (15 mg; 10%wt in alumina) as a function of temperature, with an O<sub>2</sub> / C<sub>3</sub>H<sub>8</sub> ratio equal to 6/4.

## Ni/ NiO results

As for GDC, the reduced nickel samples have been exposed to various  $O_2 / C_3H_8$  ratios at  $580^\circ C$ . Figure 4 shows the results of catalytic activity measurements obtained as a function of  $O_2 / C_3H_8$  ratio. The produced gases correspond to the reactions [1] and [2]. For mixtures rich in propane, namely from 1/9 to 4/6 ratios, carbon dioxide is the major product. The amount of carbon monoxide and hydrogen increase when the  $O_2 / C_3H_8$  ratio increases. The maximum observed in CO and  $H_2$  filled in the range 6/4 – 7/3. The  $O_2$  conversion was close to 100%. For this last ratio, for such high conversions, over-temperatures of  $15^\circ C$  could be observed, consequently to the strong exothermic reactions taking place. For ratios of 8/2 and 9/1, the catalytic activity decreased drastically, leading to practically carbon dioxide production.

The catalytic activity of  $O_2$  and  $C_3H_8$  is much higher with Ni than with GDC, especially at high temperature. Due to this comparative study, it appears that the contribution of GDC to the catalytic activity of Ni-GDC cermets for the conversion of  $O_2$  and  $C_3H_8$  mixtures into  $CO_2$  is practically negligible.

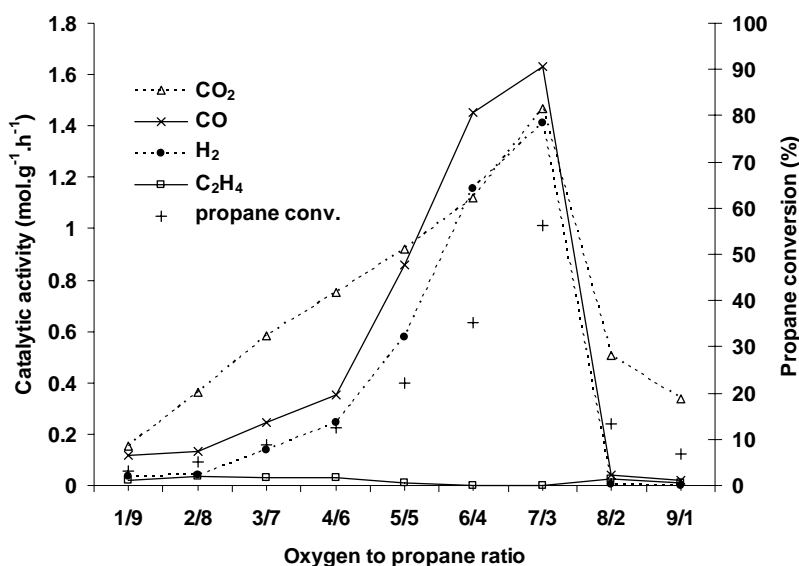


Figure 4: Catalytic activity of Ni (8 mg; 10%wt in alumina) at  $580^\circ C$ , as a function of the  $O_2/C_3H_8$  ratio.

After measurement of the catalytic activity at  $580^\circ C$  for 2 hours, (with 6/4, 7/3, 8/2 and 9/1 oxygen to propane ratio), the samples were analysed by X-Ray diffraction. Figure 5 shows the various diffraction patterns in which NiO peak at  $63^\circ$  can be easily noticed for the highest  $O_2 / C_3H_8$  ratio (9/1), and suspected for the ratio equal to 8/2. This means that in oxygen rich mixtures, metallic nickel is not stable and is oxidized into NiO. This corresponds to the drop of the catalytic activity, especially in CO and  $H_2$  (see figure 4).

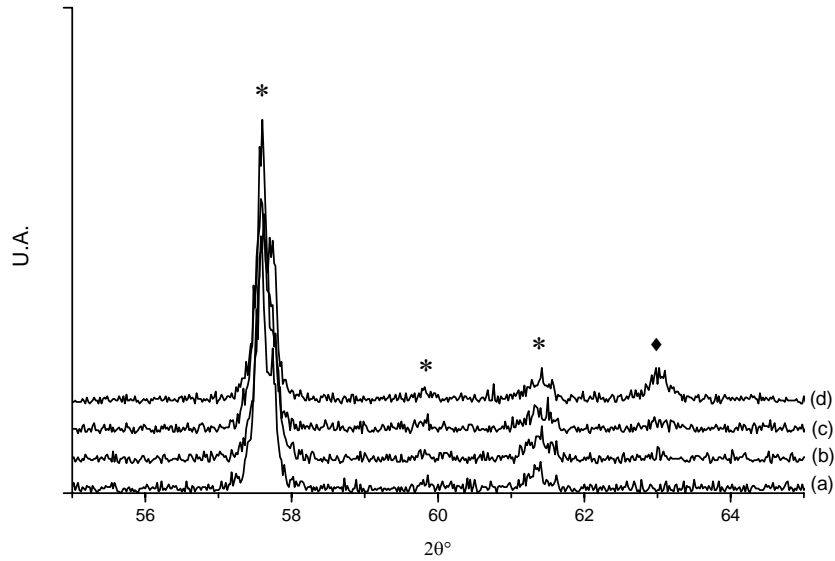


Figure 5 : XRD pattern of different samples tested at different  $O_2/C_3H_8$  ratios: (a) 6/4, (b) 7/3, (c) 8/2, (d) 9/1. \* Nickel Ni ◆ Nickel oxide NiO

As for GDC, temperature experiments have been done at various oxygen to propane ratios. Figure 6 shows the outlet gas composition as a function of temperature. The curves can be decomposed into three parts: first, below 535°C, only the total oxidation was took place leading to carbon dioxide; between 535°C and 565°C, catalyst started to promote the partial oxidation, forming CO and H<sub>2</sub>. Finally, above 565°C, all the oxygen was consumed, and the composition did not vary too much with temperature. The reproducibility is very good for low temperatures below 535°C. Above this temperature, it is still acceptable.

Such a behavior can be explained by the ability of nickel to promote the water gas shift reaction [3]



If this equilibrium occurs and reach an equilibrium state at high temperature, the values of  $K_{exp}$  defined as :

$$K_{exp} = \frac{p(CO_2)p(H_2)}{p(CO)p(H_2O)} \quad [4]$$

should be equal to those deduced from thermodynamic data ( $K_{ref}$ ).



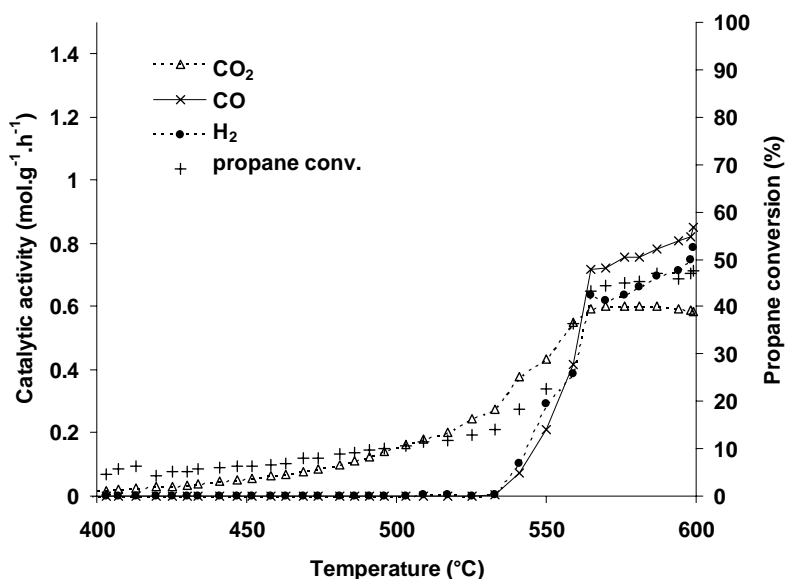


Figure 6: Catalytic activity of Ni (16 mg; 20%wt in alumina) as a function of temperature, with an  $O_2 / C_3H_8$  ratio equal to 6/4.

In our experiments, the amount of water was unknown, but from the mass balance equation upon oxygen, it could be estimated and the values of  $K_{exp}$  could be calculated at each temperature. Figure 7 displays the results obtained for  $K_{exp}$  compared to the thermodynamic prediction. It can be seen that above 570°C, the values deduced from gas analyses and mass balance are very close to those of the equilibrium constant, and follow a similar variation versus temperature, whereas it is not the case at lower temperatures. Consequently, taking into account the imprecision on the estimation of the water amount, it appears that the water gas shift equilibrium controls the gas composition above 570°C.

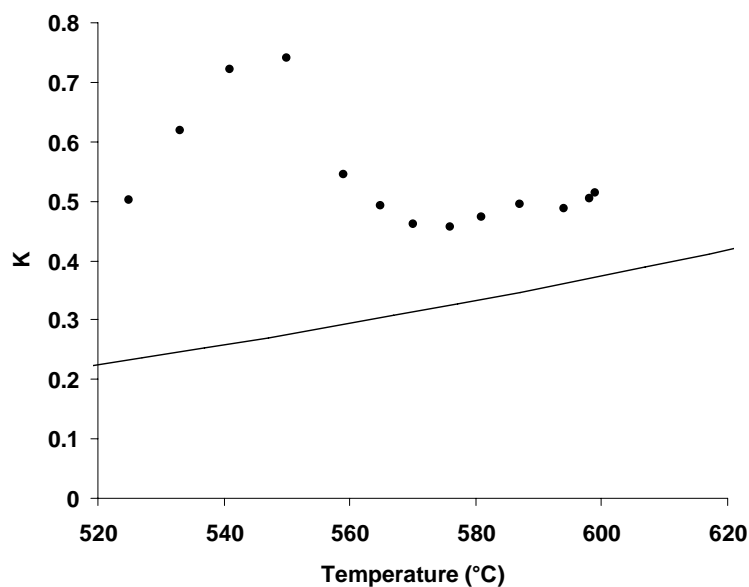


Figure 7 : Comparison between thermodynamic constant  $K$  obtained by calculation(—), and the apparent constant obtained by experimentation(●), considering water gas-shift reaction.

At lower temperatures than 570°C, the gas composition was found to change significantly with temperature. Figure 8 which represents the Arrhenius plot for carbon dioxide production, indicates the existence of two distinct values of the apparent activation energy (70 and 140 kJ.mol<sup>-1</sup>) on both sides of a limiting temperature of 520°C which is approximately the temperature at which began the production of CO and H<sub>2</sub> according to reaction [2] (partial oxidation).

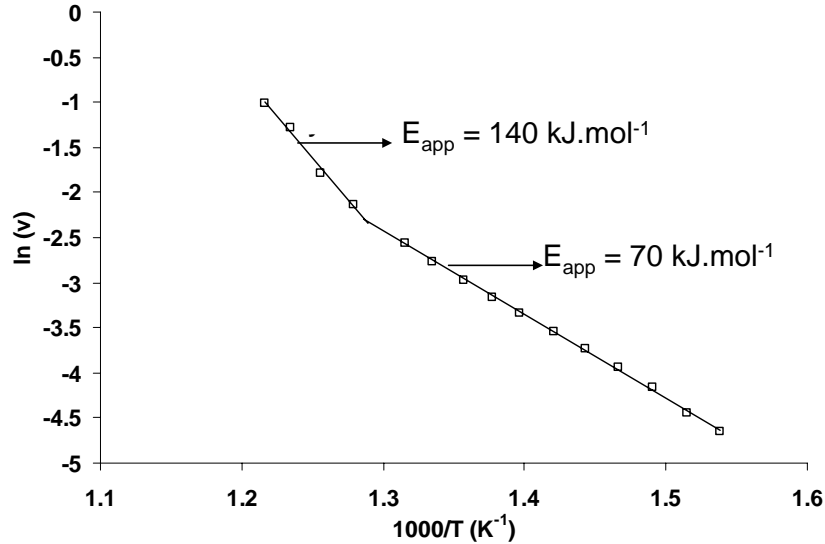


Figure 8 : Arrhenius plot of carbon dioxide production calculated from the experiment ( $O_2 / C_3H_8$  equal to 6/4)

Since CO<sub>2</sub> can only be produced by reaction [1] (total oxidation), a change in the catalyst surface must be suspected. The oxidation of nickel has already been mentioned for a temperature equal to 580°C and oxygen rich  $O_2 / C_3H_8$  ratios. Here the  $O_2 / C_3H_8$  ratio was fixed equal to 6/4, so the oxidation of nickel may be expected at a different temperature. Since XRD is not able to detect very small amounts of phases, or superficial oxidation in case of very thin layers, electrical measurements were performed on a Ni-GDC cermet.

### Electrical measurements

A 25μm thickness Ni-GDC anode, supported on GDC has been placed under a  $O_2/C_3H_8$  ratio of 6/4, in order to follow the electrical conductivity change with temperature. Figure 9 shows the total cermet conductivity and temperature, as a function of time. At the beginning of the experiment, the temperature was equal to 580°C, and metallic nickel was present due to the H<sub>2</sub> reduction treatment: value of the conductivity was as high as 800 S.cm<sup>-1</sup>. The  $O_2 / C_3H_8$  mixture was introduced, the conductivity decrease during a short period, probably due to the time necessary to reach a homogeneous mixture, and then returned to a high value of 900 S.cm<sup>-1</sup>. Temperature was set up to 590°C and then decreased stepwise down to 520°C. The conductivity remained at a high value except when the temperature was changed from 530 to 520°C where a sharp decrease was monitored. When the temperature decreases, the conductivity is quiet stable except some small oscillations. They are probably due to a carbon deposition to the

anode (black appearance of the cermet after measurements), which is a good electronic conductor.

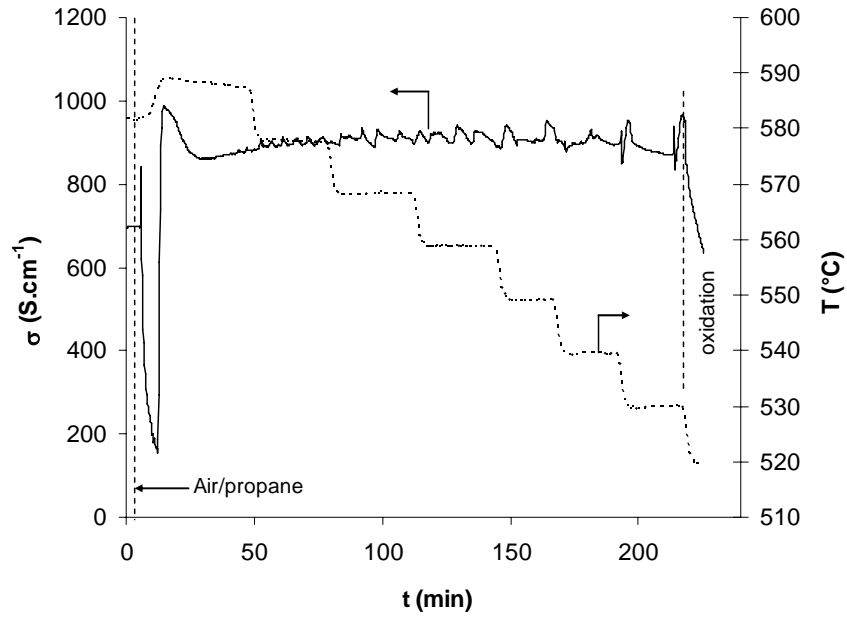
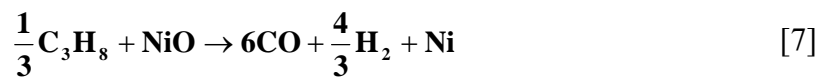


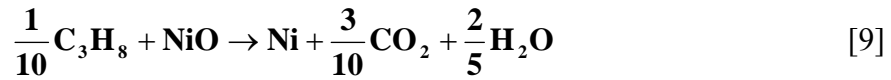
Figure 9: Ni-GDC conductivity and temperature as a function of the time under an  $O_2$  :  $C_3H_8$  : Ar (6:4:90) gaz mixture

Such a behaviour can be explained by the oxidation of nickel into NiO. The limiting temperature corresponds to that of CO and  $H_2$  production and to the different slopes in the Arrhenius plot for  $CO_2$  production. As a consequence, as far as Ni is maintained in the metallic state, CO and  $H_2$  are produced according to reaction [2]. Below a limiting temperature, which depends of the  $O_2$  /  $C_3H_8$  ratio (cf figure 5), Ni-GDC cermet is not suitable for SCFC's operation.

### Thermodynamic calculations

In order to better understand the formation of NiO below the limiting temperature, we have looked to the thermodynamics of the Ni / NiO system in a gaseous atmosphere containing oxidising ( $O_2$ ,  $H_2O$ ,  $CO_2$ ) and reducing ( $C_3H_8$ , CO,  $H_2$ ) gases. Five independent reactions may be proposed :





For each of these reactions, the reaction Gibbs energy has been calculated considering the composition of the real gas very close to 530°C, namely 535°C. As previously done, the amount of water was estimated according to the mass balance equation for oxygen. Hence,  $\Delta G^\circ(T)$  could be obtained according to the general equation [10] :

$$\Delta_r G(T) = \Delta G^\circ(T) + RT \ln \left( \frac{\prod P^{v_i}(\text{products})}{\prod P^{v_j}(\text{reactants})} \right) \quad [10]$$

where  $\Delta G^\circ(T)$  is the standard free enthalpy, R the ideal gas constant, T the temperature, P the partial pressures of the gaseous products and reactants with  $v_i$  and  $v_j$  the stoichiometric coefficients, respectively. The results are presented in figure 10 which shows the variations of  $\Delta_r G^\circ(T)$  as a function of temperature. Considering minimum  $\Delta_r G^\circ(T)$  Gibbs Energy, two reactions are expected to control the chemical state of nickel: the oxidation of Ni by oxygen [8] and the reduction of NiO by propane [7]. It can be seen that below 520°C (as indicated by the arrow), reaction [8] is the most favored reaction, whereas above 520°C, reaction [7] is the most favored. This is in very good agreement with the observed phenomenon since metallic Ni was found to oxidize at temperatures lower than 530°C.

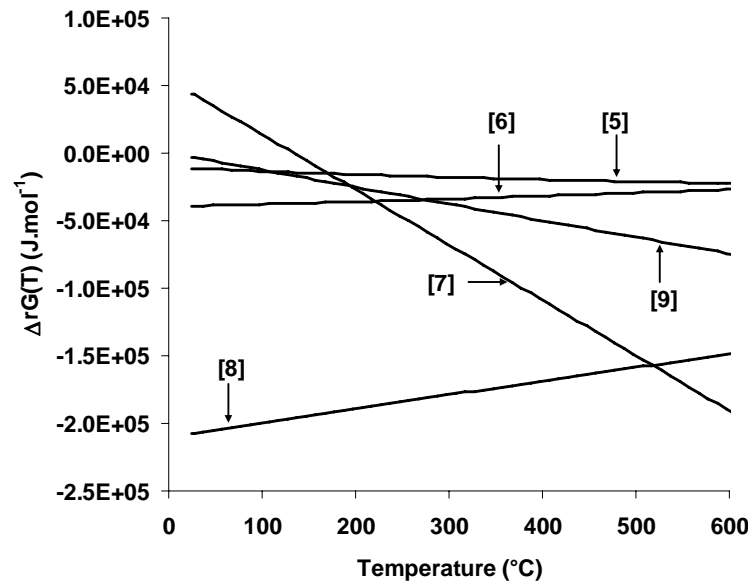


Figure 10 : Thermodynamic considerations : free enthalpy variation as a function of temperature for the different reactions involving nickel

### Conclusions

To better understand the behaviour of a Ni-GDC cermet anode working in a single chamber fuel cell under  $\text{O}_2 / \text{C}_3\text{H}_8$  mixtures, the catalytic properties of GDC and nickel

powders were studied separately as a function of the oxygen to propane ratio and of temperature.

The GDC powder was found to catalyze the total oxidation of propane [2] in the range 400-600°C. However, even at high temperatures, the catalytic activity was not very high compared to that of nickel in similar conditions.

Nickel was found to catalyze also partial oxidation of propane [1]. The maximal amounts in CO and H<sub>2</sub> were obtained for O<sub>2</sub> / C<sub>3</sub>H<sub>8</sub> ratios close to the stoichiometric proportions.

The catalytic activity versus temperature showed three domains which temperature limits way depend on the O<sub>2</sub> / C<sub>3</sub>H<sub>8</sub> ratio. For a ratio equal to 6/4:

- above 565°C, the water gas shift equilibrium controls the gaseous composition,
- between 535°C and 565°C, simultaneous total and partial oxidation occurred,
- below 535°C, only total oxidation took place due to oxidation of nickel into NiO in agreement with thermodynamic prediction.

This study not only clarifies the nature of the reactions involved in the SCFC's operated with O<sub>2</sub> / C<sub>3</sub>H<sub>8</sub>, but also points out the existence of a limiting temperature. Above this limiting temperature, metallic nickel is stable and the anode is able to provide CO and H<sub>2</sub> at sufficient rates. However, the temperature must not exceed too high values since once the water gas shift equilibrium is reached, the gas composition does not vary too much. Studying the catalytic activity of nickel for CO and H<sub>2</sub> production allows to determine the best compromise with respect to temperature.

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